Electronic Supplementary Information (ESI) for:

Halochromic and Hydrochromic Squaric Acid Functionalized Perylene Bisimide

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1. Materials and methods

N,N-Dicyclohexyl-1,7-dibromoperylene-3,4:9,10-tetracarboxylic acid bisimide (1)¹ and 3-(1-methyl)ethyloxy-4-(tributylstannyl)cyclobut-3-ene-1,2-dione $(4)^2$ were prepared according to the literature. All commercial reagents and solvents were used as received without further purification. Silica gel (Silica 60M; particle size: 0.040-0.063 mm) for the purchased from Merck (Hohenbrunn. flash chromatography was Germany). Spectroscopic-grade solvents were purchased from Merck and VWR Int. (Darmstadt, Germany) and used for spectroscopic measurements. NMR spectra were obtained using a Bruker DMX 400 or JEOL ECX-400 spectrometer operating at 400 MHz for ¹H NMR and 100 MHz for ¹³C NMR. Chemical shifts were reported in parts per million (δ) downfield from tetramethylsilane (TMS) as an internal standard in $CDCl_3$ or $DMSO-d_6$. The IR spectra were recorded using a Shimadzu FT-IR 8400S spectrophotometer. The electrospray ionization mass spectra (ESI-MS) were recorded on a JEOL JMS-T100CS spectrometer. The elemental analyses were performed on a J-Science Lab CHN CORDER JM-10 analyzer (Kyoto, Japan). The absorption spectra were measured in 0.1, 0.5, or 1.0 cm quartz cells on a Perkin Elmer Lamda 950, Lamda 35, Lamda 40P UV/vis spectrometer, a Shimadzu UV-3100 spectrophotometer and a JASCO V-630 spectrophotometer. pH values of aqueous solution were measured on a Horiba pH meter D-12 equipped with a glass body sleeve electrode 6377-10D. The relative humidity was monitored using an Ohm Electronics HB-T01-W thermo-hygrometer (Saitama, Japan)

2. Synthesis and characterization of PBIs bearing cyclobutenedione moieties

Preparation of perylene bisimide 2

In a two-necked round-bottom flask, *N*,*N*-dicyclohexyl-1,7-dibromoperylene-3,4:9,10tetracarboxylic acid bisimide **1** (0.50 g, 0.70 mmol) was dissolved in 120 mL of degassed toluene under a N₂ atmosphere. To the solution were added 3-(1-methyl)ethoxy-4-(tributylstannyl)cyclobut-3-ene-1,2-dione 4 (1.30 g, 3.0 mmol), Pd(PPh₃)₄ (0.20 g, 0.18 mmol), and CuI (0.065 g, 0.34 mmol) under a N₂ flow, and the mixture was stirred at 100 °C for 3 h. After cooling down to room temperature, the solvent was removed under reduced pressure and the residue was added to a large amount of hexane to precipitate the PBI derivative. The precipitate was collected by filtration and then purified by silica gel column chromatography (eluent; CH₂Cl₂/diethylether 100/0 - 20/1, v/v). After removal of eluent, the residue was further purified by precipitation through slow diffusion of its concentrated CH₂Cl₂ solution into n-hexane. The product **2** was obtained as a dark-red solid (0.41 g, 70%). ¹H NMR (CDCl₃, 400 MHz): δ 9.05 (s, 2H), 8.63 (d, J = 8.0 Hz, 2H), 8.05 (d, J = 8.0 Hz, 2H), 5.82-5.73 (m, 2H), 5.10-4.99 (m, 2H), 2.65-2.46 (m, 4H), 2.01-1.86 (m, 4H), 1.86-1.69 (m, 6H), 1.60 (d, J = 6.0 Hz, 12H)), 1.58–1.25 (m, 6H). ¹³C NMR (CDCl₃, 100 MHz): δ 194.6, 192.2, 189.6, 176.0, 163.3, 163.2, 134.3, 133.2, 131.5, 130.7, 130.4, 128.5, 127.6, 123.9, 123.8, 82.0, 54.4, 29.2, 26.5, 25.4, 23.1. IR (KBr, cm⁻¹): 2926, 2921, 1779, 1745, 1698, 1658, 1590, 1455, 1422, 1417, 1330, 1258, 1240, 1092. HRMS (ESI): m/z calcd for $[M(C_{50}H_{42}N_2O_{10})]^-$, 830.2839; found 830.2832. Anal. Calcd for $C_{50}H_{42}N_2O_{10}$: C, 72.28; H, 5.10; N, 3.37. Found: C, 72.24; H, 5.06; N, 3.19%.

Preparation of perylene bisimide 3

PBI 2 (0.050 g, 0.060 mmol) was dissolved in a mixture of THF and 6 M aqueous HCl (THF/HCl aq., 30/1(v/v), 26 mL) and then stirred at 50 °C for 25 h. After cooling down to room temperature, the solvent was removed under reduced pressure. The residue was purified by precipitation through slow diffusion of its CH₂Cl₂/MeOH (95/5(v/v), 1 mL) solution into a large amount of diethylether. The product **3** was obtained as a black solid (0.042 g, 94%). ¹H

NMR (DMSO- d_6 , 400 MHz): δ 9.28 (s, 2H), 8.34 (d, J = 8.2 Hz, 2H), 8.11 (d, J = 8.2 Hz, 2H), 5.02–4.88 (m, 2H), 1.98–1.64 (m, 12H), 1.51-0.98 (m, 8H). ¹³C NMR (CDCl₃, 100 MHz): δ 215.4, 194.2, 176.3, 163.4, 163.2, 134.9, 129.5, 129.4, 129.2, 128.0, 127.3, 127.2, 126.2, 122.2, 120.9, 52.8, 28.5, 26.1, 25.2. IR (KBr, cm⁻¹): 3431, 2930, 1761, 1684, 1601, 1583, 1419, 1330, 1258, 1246. HRMS (ESI): m/z calcd for [M(C₄₄H₃₀N₂O₁₀)-2H]²⁻, 372.0872; found 372.0879. Anal. Calcd for C₄₄H₃₀N₂O₁₀ • 4H₂O: C, 64.54; H, 4.68; N, 3.42. Found: C, 64.68; H, 4.58; N, 3.17%.

3. pH-dependent absorption spectra of PBI 3 bearing the 2-hydroxycyclobutenedione moiety in water-THF.

PBI **3** (1.5 mg, 2.0×10^{-3} mmol) was dissolved in a water-THF mixture (20 mL, 15/85 (v/v)). The pH and absorption spectrum of the solution were measured using a Horiba LAQUA 6377-10D pH meter and Jasco V-630 spectrophotometer with a 1.0-cm cell, respectively. The pH conditions from pH 5.5 to pH 1.2 were obtained using 7.5 μ L of 0.5–12 M HCl aqueous solution. The lower pH values (< 1.2) were accomplished by the addition of 15–480 μ L of aqueous HCl solution. The pH and absorption spectrum of the resulting solution were measured at 25 °C after the addition of a certain amount of HCl. Figure S1 shows the absorption spectra of **3** solution under various pH conditions. In the water-THF (15/85) mixture, **3** showed a broad absorption spectrum with a maximum at 635 nm, which resembled the absorption spectrum of **3**^{2–} produced by the addition of Hünig's base. Thus, water is sufficiently acidic to promote the deprotonation of **3**. The absorption at 635 nm was decreased and the S₀-S₁ absorption at 575 nm was increased with the decrease of pH value. The plot of absorbance at 635 nm *vs* pH value, along with the fitted curve, is shown in Fig. S1. The change of the absorbance proceeded in two steps which can be related to the diacid structure **(Scheme S1)**.

Scheme S1. Acid/base equilibrium of PBI 3.



The acid dissociation constant (pK_a) for **3** in water/THF was estimated by the curve fitting according to the following equation:

$$A_{635 nm} = \frac{A_3 + K_{a1} \cdot 10^{pH} \cdot A_{3^-} + K_{a1} \cdot K_{a2} \cdot 10^{pH} \cdot 10^{pH} \cdot A_{3^{2^-}}}{1 + K_{a1} \cdot 10^{pH} + K_{a1} \cdot K_{a2} \cdot 10^{pH} \cdot 10^{pH}}$$

where K_{a1} and K_{a2} are the acid dissociation constants for each proton dissociation of diacidic **3** and A_3 , A_{3^-} , and $A_{3^{2^-}}$ represent absorbances of **3**, **3**⁻, and **3**²⁻, respectively. The plateau in the plot was used to derive the absorbance values of **3**²⁻ (1.67) and **3**⁻ (1.42) and the obtained pK values are $pK_{a1} = -0.3$ and $pK_{a2} = 2.7$. The lower pK_{a1} is almost similar to the one previously reported for hydroxycyclobutenes, whilst the value of pK_{a2} is significantly higher.³ Squaric acid exhibited a two-step dissociation of acidic protons in aqueous solution, where pK values are reported as 0.6 for pK_1 and 3.48 for pK_2 .⁴ The acid strength was given by the stabilized enolate and dienolate structures.⁵ The two-step dissociation of **3** observed in aqueous THF might be also explained by a stabilization of **3**⁻ through delocalization along the PBI scaffold.



Fig. S1 (A) pH-dependent absorption spectra of **3** in water-THF (3/17(v/v), 1×10^{-4} mol/L, 25 °C). Arrows indicate changes upon addition of aqueous HCl . Absorption spectra of the initial solution of **3** (pH 5.5) and after the addition of excess aqueous HCl (pH -0.9) are displayed as blue and red lines, respectively. (B) Plot of absorbance at 635 nm *vs* pH observed using the pH meter and fitting of the data points to the above equation.

4. Halochromic effect of 3 in various solvents with additives

The PBI bearing squaric acid residues (**3**) showed a halochromic property in various solvents. As shown in Fig. 2, the addition of Hünig's base resulted in a bathochromic shift of the absorption band in THF. In acetone, a similar change of the absorption spectra of **3** upon addition of Hünig's base was observed (**Fig. S2A**). In methanol PBI **3** showed already the absorption maxima at longer wavelengths in comparison to those in THF and acetone. The addition of an excess amount of Hünig's base resulted therefore in only a minor spectral change. In contrast, the absorption maximum of **3** was significantly changed by mixing with an excess amount of TFA, suggesting that **3** existed in its conjugated base form in methanol and was regenerated by the aid of TFA (Fig. S2B). The data of the absorption maxima are summarized in two categories involving the acid form and the conjugated form in **Table S1**.



Fig. S2 (A) Changes in the absorption spectra of **3** in acetone $(2 \times 10^{-4} \text{ M}, 25 \text{ °C})$ upon addition of Hünig's base (0–2.5 equiv. vs **3**). The absorption spectra of the initial solution and the solution after addition of excess amounts of Hünig's base (2.5 equiv.) are displayed as red and blue lines, respectively. (B) Changes in the absorption spectra of **3** in methanol $(2 \times 10^{-4} \text{ M}, 25 \text{ °C})$ upon addition of TFA (0–1000 equiv. vs **3**). The absorption spectra of the initial **3** and after addition of excess amounts of TFA (1000 equiv.) are displayed as blue and red lines, respectively. Arrows indicate changes upon the addition of acid or base.

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Species	Solvent	Additive	λ_{\max} , (log ε) /nm
Acid form	THF	non	329 (4.56), 569 (4.45)
	Acetone	non	328 (4.41), 565 (4.23)
	Methanol	TFA	326 (4.36), 566 (4.29)
	Water/THF ^b	HCl aq.	344 (4.41), 576 (4.28)
Conjugated base	THF	Hünig's base	359 (4.59), 641 (4.32)
	Acetone	Hünig's base	363 (4.45), 623 (4.10)
	Methanol	non	350 (4.44), 612 (4.25)
form	DMF	non	367 (4.52), 667 (4.20)
	DMSO	non	368 (4.55), 667 (4.25)
	Water/THF ^b	non	360 (4.41), 632 (4.20)
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Table S1. Absorption maxima of 3 in various solvents with additives^{*a*}

^{*a*}Absorption spectra were measured in the given solvents $(2 \times 10^{-4} \text{ M})$. ^{*b*}The concentration was set at 1×10^{-4} M and the water/THF ratio was 15/85(v/v).

5. Absorption and ¹H NMR spectra of 3 upon dilution in THF

The weak absorption observed in THF from 600 to 700 nm was enhanced upon dilution (Fig. S3). This result rules out the possibility that the broad absorption originated from the aggregation of 3, because aggregation is promoted at higher concentrations. Instead, this result indicates that the content of impurities such as water affected the absorption properties of 3. The ¹H NMR spectra of 3 under various concentrations and the addition of Hünig base provided information on the origin of the spectral changes (Fig. S4). The singlet at 9.02 ppm attributable to the aromatic protons at 2,8-positions (ortho positions neighboring to the cyclobutene substituents) of **3** is shifted to lower field with decreasing concentration. On the other hand, the two doublet of 5,11- and 6,12-protons at 8.30 and 8.50 ppm are shifted to higher field. Furthermore, the color of the diluted THF solution $(1 \times 10^{-5} \text{ M})$ turned to blue. A set of signals of THF solution with 30 equivalents of Hünig base was observed at almost the same chemical shifts as under the dilution condition. There is no broadening of signals and/or appearance of complicated signals, indicating that no aggregation of **3** takes place under these conditions. As expected from the similarity of the spectral changes in water and acid/base addition, 3 is deprotonated and exists as its conjugated base at the lower concentration because of residual water in the solvent.



Fig. S3 Absorption spectra of 3 at different concentrations in THF (2×10^{-4} , 2×10^{-5} , 2×10^{-6} M).



Fig. S4 ¹H NMR (25 °C, THF- d_8) spectra of **PBI-OH** at 10^{-3} M (a), 10^{-4} M (b), 10^{-5} M (c), and with Hünig's base (30 equivalents, [**PBI-OH**] = 10^{-4} M). Signals marked with an asterisk are impurities present in THF- d_6 .

6. Color change of a PEG thin film doped with 3 by the exposure to humid air

The PEG film doped with PBI **3** was spin-coated onto a quartz substrate, which was cleaned with isopropyl alcohol, at 1000 rpm from a homogeneous chloroform solution of PEG (M_w 2000, hydroxyl-terminated, Kishida Chemical Inc., Tokyo, Japan) and PBI **3** with weight ratio of 5 : 2. The PBI **3**-loaded PEG film was exposed to the breath to display the response to humid air (**Movie S1**).



Movie S1 Color change of a PEG thin film doped with PBI 3 upon the exposure of the breath as typical humid air.

The absorption spectral change of the PEG thin film doped with PBI **3** upon different humidity level was measured using a JASCO V-630 spectrophotometer which was placed in a small chamber (**Fig. S5**). The relative humidity (RH) in the chamber was monitored by a thermo-hygrometer. The absorption spectrum of the dried film is almost identical to that of the film in the RH of 40%. The absorption at 650 nm was increased with increased humidity levels up to RH of 90%. The absorption was dropped in the RH of 95% probably due to the dew drop.



Fig. S5 Absorption spectra of the PEG thin film doped with PBI **3** in the relative humidity of 40% (red), 50% (orange), 60% (green), 70% (blue), 90 (purple), and up to 95% (gray).

7. Optimized structures of 3 and 3²⁻ obtained through DFT calculations

Optimized structures of **3** and 3^{2-} were obtained by DFT calculations at the rB3LYP/6-31+G(d) level of theory to gain insight into their molecular structure and electron distributions (**Fig. S6**).⁶ In the optimized geometry of **3**, the perylene skeleton is twisted along the waistline of the PBI bay area with a dihedral angle (θ) of 26°, which is slightly larger than those reported for other twofold bay-disubstituted PBIs (e.g., θ up to 15° for 1,7-diphenoxy-PBI),⁷ leading to a broader absorption band with less pronounced vibronic fine structure. The calculation of 3^{2-} which was performed using **3** with optimized geometry as an initial structure showed that the perylene skeleton is distorted similarly with an angle of 25°. According to these calculations, the deprotonation of **3** affected the distorted structure of the perylene core only to a minor extend and therefore the observed changes in absorption properties can be safely related to electronic effects.



Fig. S6 Optimized structures of 3 (A) and 3^{2-} (B) obtained by DFT calculations. Colored squares represent planes including naphthalene rings in PBI cores.

8. NMR and MS spectra



Fig. S7 ¹H NMR (400 MHz) spectrum of PBI 2 in CDCl₃.



Fig. S8 ¹³C NMR (400 MHz) spectrum of PBI 2 in CDCl₃.



Fig. S9 ¹H NMR (400 MHz) spectrum of PBI 3 in DMSO- d_6 .



Fig. S10 13 C NMR (400 MHz) spectrum of PBI 3 in DMSO- d_6 .



Fig. S11 ESI-MS spectrum of PBI 2.



Fig. S12 ESI-MS spectrum of PBI 3.

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